

BELLCOMM. INC.

1100 Seventeenth Street, N.W. Washington, D. C. 20036

SUBJECT: Preliminary Findings--Flame
Propagation Dependence on Atmos-
pheric Oxygen - Case 320

DATE: July 23, 1968

FROM: S. S. Fineblum

ABSTRACT

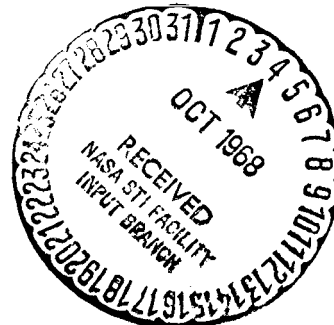
Flame propagation data for many solids in a wide range of atmospheres show that the assumption of a simple power-law dependence of flame propagation velocity on the oxygen partial pressure or concentration is not accurate. The materials tested show a steep rise of flame speed from zero propagation with added oxygen, a reduced slope at moderately enriched concentrations, and another distinct rise at higher concentrations. The non-linear influence of oxygen concentration on pyrolysis rates (as shown by Thermogravimetric Analysis) and the non-linear influence of flame temperature on heat transfer all contribute to the observed non-linearity of flame spread over solids. Pyrolysis data with proper analysis of these related processes may provide the physical basis for a rational model for predicting flame spread.

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Flame propagation data for many solids in a wide range of atmospheres show that the assumption of a simple power-law dependence of flame propagation velocity on the oxygen partial pressure or concentration is not accurate. The materials tested show a steep rise of flame speed from zero propagation with added oxygen, a reduced slope at moderately enriched concentrations, and another distinct rise at higher concentrations. The non-linear influence of oxygen concentration on pyrolysis rates (as shown by Thermogravimetric Analysis) and the non-linear influence of flame temperature on heat transfer all contribute to the observed non-linearity of flame spread over solids. Pyrolysis data with proper analysis of these related processes may provide the physical basis for a rational model for predicting flame spread.

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MEMORANDUM FOR FILE

The well known stimulation of flame propagation along solids by an increase of oxygen concentration in the environment has not yet been expressed accurately. That is, there is no dependable basis for predicting the variation of flame spread velocity with oxygen concentration. It is important that this variation be predictable so that the flame propagation velocity associated with a material at one oxygen concentration may be reliably estimated from propagation measurements at other concentrations. This capability would permit the more systematic selection of materials for use in spacecraft, submarines, test chambers, diving equipment and other inhabited systems with enriched oxygen atmospheres, and would also contribute to a more precise balance of flammability and other hazards in the selection of the oxygen concentration for such chambers.

This report points out that a simple power law correlation is inaccurate and that instead the flame propagation rate characteristically shows a non-linear dependence on oxygen concentration. It is suggested that the similarity between the influence of oxygen concentration on pyrolysis and on flame propagation may mean that thermogravimetric analysis (pyrolysis) data can help to predict flame propagation rates.

SIMPLE POWER LAW DEPENDENCY

The correlation between flame spread velocity and oxygen concentration has often been approximated by a simple power law dependency (1-5),

$$r \sim (O_{2MF})^m \quad 1a$$

$$\text{or } r \sim (O_{2MF}^m)^{m'} \quad 1b$$

$$\text{or } r \sim (O_{2MF}^P)^m \quad 1c$$

where r is the flame propagation velocity, O_{2MF} the mole fraction

of oxygen, P the pressure, and m and m' constants of the material. This simple dependency is usually supported by a log-log plot of flame-spread-rate data. Such log-log plots tend to mask curvature, however, thus giving an impression of (logarithmic) linearity. Closer examination of the data shows that no simple power law can achieve the precise correlation claimed. Firstly, the simple power law equations presented above cannot predict the concentrations which result in zero flame propagation. Secondly, the slope of flammability versus oxygen concentration changes much too severely and unevenly for a precise representation by any simple power law.

As demonstrated by the experimental data on sheets 1 to 3*, the typical flame spread rate increases sharply from zero, and then increases again at the high oxygen concentrations. It is significant that these similar curves:

- a. represent the experimental data of 12 very dissimilar materials (paper, cotton, rubber, Teflon, Nomex, etc.)
- b. are from four different sources with wide variations in specimen dimensions and ignition techniques.
- c. increase in log-log nonlinearity with the number of data points.

This uneven increase of flame spread velocity, as indicated by the inflections in the curves, was noted by E. M. Roth (8), and recently by A. H. Striepen (9). Robinson and Gross of National Bureau of Standards also noted a similar response of burning rate in an enclosed chamber with an increase in ventilation (10). This increase in ventilation increased the overall supply of oxygen and decreased the concentration of products of combustion. Oxygen concentration available at the flame front in this case was roughly proportional to the ventilation.

Figure 12* on sheet 3 is especially instructive on the non-power-law dependency of flame propagation. This figure is a modification of Figure 12 from the comprehensive experimental report by Kuchta, et al of the Bureau of Mines (1). Zero-flame-spread points from this same report and others (7, 13) were added and curves were drawn through the experimental

* Also see Kimzey (6) and Chianta and Stoll (7).

points. These curves of flame-spread versus oxygen-partial-pressure have the same characteristic shape as other curves based on oxygen mole fraction alone. This is as one would expect for constant pressure enrichment where partial pressure is proportional to mole fraction or for cases where the total pressure influence is comparatively weak (1).

The curves of upward burning and downward burning are different in two respects: shape and scale. The upward flame velocity seems to level off at very high concentrations as shown on sheet 2. The downward velocity continues to increase at a steep and increasing rate as shown on sheet 1. Secondly, the upward burning rate is much greater. In comparisons reported (1,5,9) upward burning was 3 to 15 times as rapid as downward or horizontal burning. Some flame resistant materials, for instance 10-mil Teflon and 40-mil silicone-resin-laminate, would propagate only if ignited at the bottom and permitted to burn upward (9). This is expected because upward burning is accelerated (during normal positive-"g" burning) by the upward flow of hot gases which engulf and preheat the as-yet-unburned solid above the rising flame front.

AN IMPROVED POWER LAW DEPENDENCY

An improvement over the simple power law dependency which is capable of predicting zero flame spread rate has been proposed by the investigators at Atlantic Research Corporation (11).

"The burning rate of filter paper in the upward direction at a 45° angle in the normal gravitational field is well correlated by the equation,

$$r = 4.6 \log \left\{ P^{0.5} / \left[(C_P)_{O_2} + n(C_P)_x \right] \right\} + 7.8$$

over the pressure range from 0.2 atm to 10 atm and for gas compositions from pure oxygen to oxygen diluted with up to 80 percent nitrogen or helium. Here r is the flame spread rate in cm./sec., P is the pressure in atmospheres, n is the number of moles of inert gas per mole of oxygen, and C_P is the heat capacity at constant pressure for oxygen or the inert gas."

The first term is analogous to the simple power law equation, lb , and the constants are functions of the material. In general,

$$r = a \log \left\{ P^m / \left[(C_P)_{O_2} + n(C_P)_x \right] \right\} + b \quad (2)$$

where a , b , and m are constants for the material and direction of burning.

The effect of the inert gas as a thermal sink that deprives the combustion process of heat is included in this equation. Although a rigorous theory relating heat loss to the surrounding gas and a decrease in flame propagation is not yet available, it has been shown to be reasonable. For example, the relative effectiveness of high over low molar specific heat inerting agents (N_2 versus He) has been demonstrated (4,12).

The first term is, for most practical conditions, less than unity and the log is therefore negative. The condition of zero flame spread can thus be predicted when the first negative term and the second positive term, b , are equal,

$$a \log \left\{ P^m / \left[(C_P)_{O_2} + n(C_P)_x \right] \right\} = b \quad (2')$$

As stated by Huggett, et al, this improved form of the power law shows better correlation with experimental data than the simple power law (11). However, the fit of this equation also becomes less satisfactory as the range and the number of experimental points increases. For example, equation 2 was compared with typical experimental results reported by the NASA Manned Space Center (17) on the combustion of .005-inch Nomex. As seen on sheet 5, the rate of flame spread can be approximated from 30 to 100% oxygen when the coefficients a , b , and m were 0.61, 0.815, and 0.50 respectively. The experimental propagation velocity at high concentrations, however, increases with a concave upward rather than the concave downward slope indicated by Equation 2.

If a , b , and m were permitted to vary with oxygen concentration, the resulting curve could be made to fit this or any other similar data. In general, it is possible to approximate the actual flame spread velocity as

$$r = f_a (O_{2MF}) \log \left[P^{fm} (O_{2MF}) / \left\{ (C_P)_{O_2} + n(C_P)_x \right\} \right] + f_b (O_{2MF}) \quad (3)$$

where the functions of the oxygen mole fraction f_a , f_m , and f_b are substituted for the constants a , m , and b , respectively, in Equation 2. The pressure exponent f_m (O_{2MF}) for example approaches zero and sometimes becomes negative; examples of its variation are shown on sheet 4 and elsewhere (12-16). By proper choice of the function f_b the concave-upward response of sheet 5 can be predicted.

It should be emphasized that Equation 3 may not be the best expression. For example, the sudden changes in response suggest, as one alternative, a sum of functions having Heaviside unit functions as multipliers.* The accuracy and usefulness of any such equations are limited to the quantity and quality of experimental points for each material, however. The important need is not an improved curve fitting procedure. What is required is the understanding to permit the formation of a reasonable model of flame spread and the influence of oxygen concentration.

POTENTIAL USE OF PYROLYSIS DATA TO PREDICT FLAME PROPAGATION RATES.

The dominant processes in flame propagation are heat transfer, pyrolysis, and combustion. Heat transfer from the ignition source to the solid fuel starts combustion by supplying sufficient heat to initiate pyrolysis, which is the liberation at high temperature of gases and vapors by thermal decomposition of the solid chemical structure. These pyrolysis products when sufficiently heated will exothermally combine with available oxygen in the combustion process. This combustion process is the source of the required heat to pyrolyze the adjacent not-yet-burning solid. Thus, the flame acts as the ignitor in the continuous process of gas-phase ignition required for flame propagation (2,19,20). Each of these processes, heat transfer, pyrolysis and combustion, is sensitive to the gaseous environment and temperature; all are known to be nonlinear.

The Thermogravimetric Analysis (TGA) of many materials shows that the weight loss due to pyrolysis increases nonlinearly with temperature, as illustrated on sheet 6 and elsewhere (24). It is well-known that (until the mixture at the front becomes fuel lean) an increase in oxygen concentration

* Heaviside unit function $H(x-x_1)$ goes from 0 to 1 when $x-x_1$ changes from negative to zero as a variable approaches and then goes beyond the fixed interval $x-x_1$. Thus, various functions can be phased in (or out) when entering (or leaving) their interval of effectiveness. For instance, $H(x-x_1)$ goes from 0 to 1 at $x-x_1$ and $H(x_2-x)$ drops from 1 to 0 at x_2 and beyond.

generally causes an increase in flame temperature. Since pyrolysis is governed by the flame temperature, and flame temperature by oxygen concentration (see sheet 7), pyrolysis during combustion depends upon oxygen concentration. Hence it seems reasonable to relate the abscissa indication of temperature to a roughly proportional scale of oxygen concentration.

In addition, the time lag between the instantaneous mass loss and equilibrium mass loss is also a function of the temperature as shown in Figure 13 on sheet 8. This time lag which is important during the rapid heating of solids (as during actual fires) can similarly be shown to be a function of the oxygen concentration. Further, the mass rate of pyrolysis which converts the solid to combustible gases and vapors at constant heating rate is directly related to the rate of steady state flame propagation:

$$r = \frac{\dot{m}_p}{\rho A} \quad (4)$$

where \dot{m}_p is the mass rate of pyrolysis and ρ and A are the mass of pyrolyzing components per unit volume and cross sectional area of the burning solid, respectively. Therefore, the ordinate indication of mass loss by pyrolysis might be replaced by a proportional ordinate indication of flame propagation rate. Thus, data on the nonlinear response of pyrolysis with temperature may be of help in the interpretation of the similar non-linear response of propagation rate with oxygen concentration.

The details of this response, as well as the response of flame temperature to oxygen concentration, combined with heat transfer from the flame to the as-yet unburned solid are essential ingredients for the required combustion model. When available, it should be possible to predict the nonlinear response of flame propagation to oxygen enrichment and possibly other environmental factors (pressure, acceleration, etc.) as well. Progress toward such a model can now be observed (18,19, 20 and 21).

CONCLUSIONS

It is clear from the data of solid fuels burning in oxygen-bearing atmospheres that: (1) The flame spread velocity increases in a distinct, but highly non-linear (and non-power law) manner. As more precise experimental data are generated the response may prove to be even more complex than indicated by the limited data now available. (2) Typically, the flame velocity increases dramatically as oxygen content goes up just above the point of minimum oxygen for support of combustion, and then rises sharply again with high oxygen concentration. (3) In addition, burning downward and burning upward differ in that the downward flame velocity continues to increase up to

100% oxygen, while upward flame velocity seems to level off just below 100%. (4) The non-linear dependence of pyrolysis on oxygen concentration and the heat transfer dependence on flame temperature may, with proper analysis, become the physical bases for a rational model.

It is important that a rational and more complete model relating the heat transfer, pyrolysis and combustion processes to flame propagation be the basis for future attempts at achieving correlations with experiment. It is equally important that such attempts be enriched with increased data on pyrolysis and propagation rates of identical samples tested under standardized conditions.



S. S. Fineblum

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Attachments

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Sheets 1-8

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DOWNWARD BURN RATE, IN/SEC.

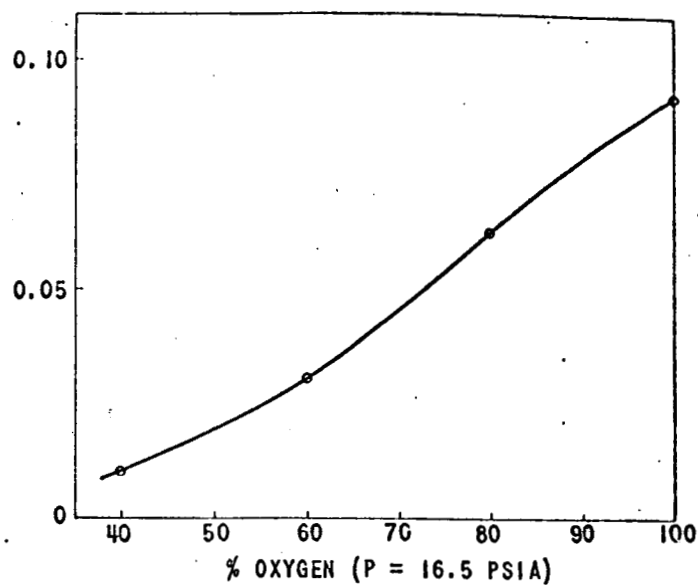


FIGURE 2 - COMBUSTION RATE OF RTV 560/577 (85/15) SILICONE ELASTOMER BLEND (0.125-IN. THICK) (REF. 9)

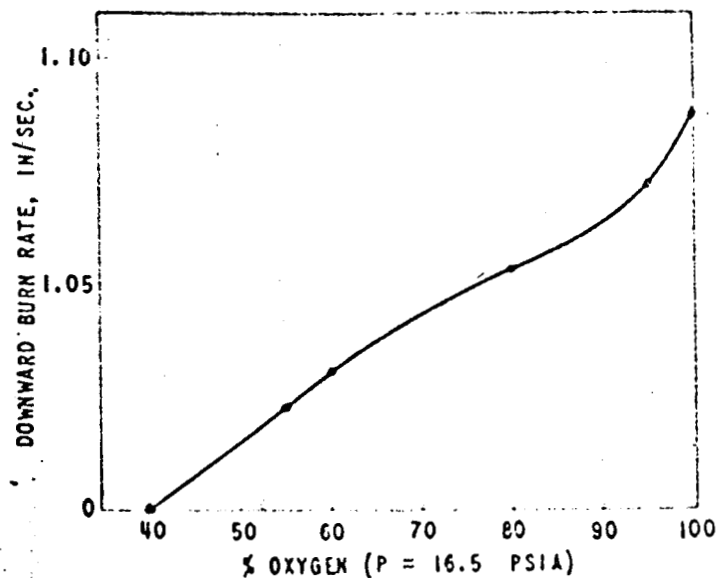


FIGURE 3 - COMBUSTION RATE OF RL 2060 FLUOREL SPONGE (0.23-IN. THICK) (REF. 9)

FIGURE - DOWNWARD PROPAGATION OF 0.005 INCH NOMEX IN VARIOUS O_2/N_2 MIXTURES AT A TOTAL PRESSURE OF 16.5 PSIA

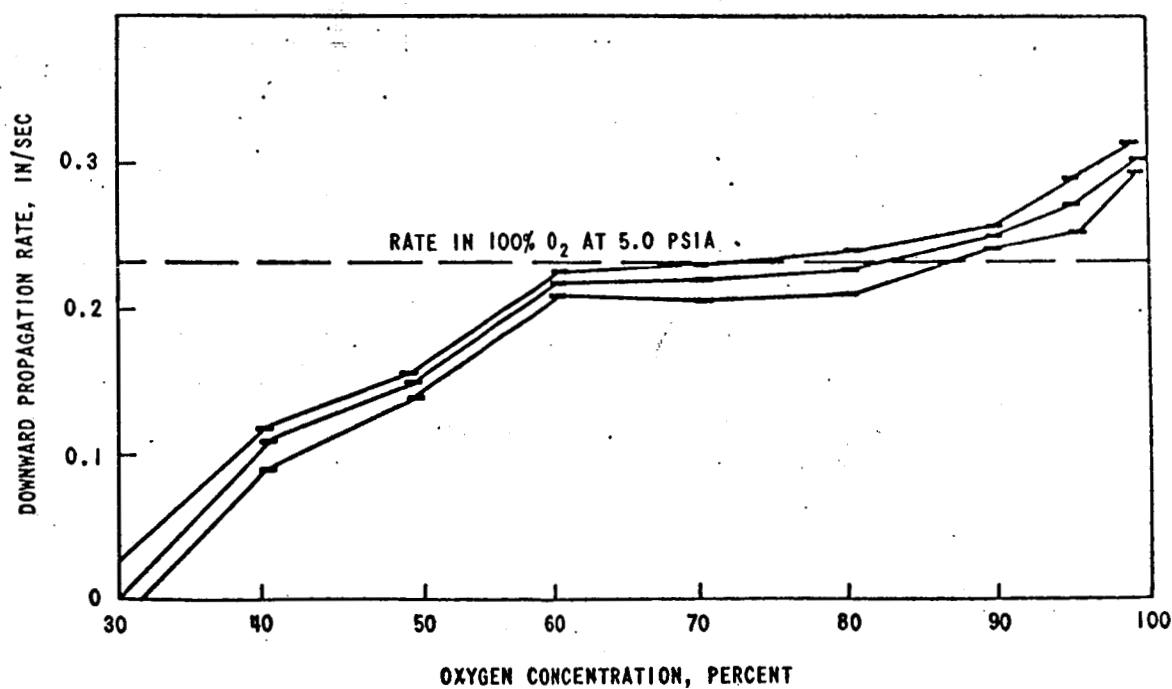


FIGURE 4 - COMBUSTION RATE OF TEFLON,
TYPE E-7A (10-MILS THICK)

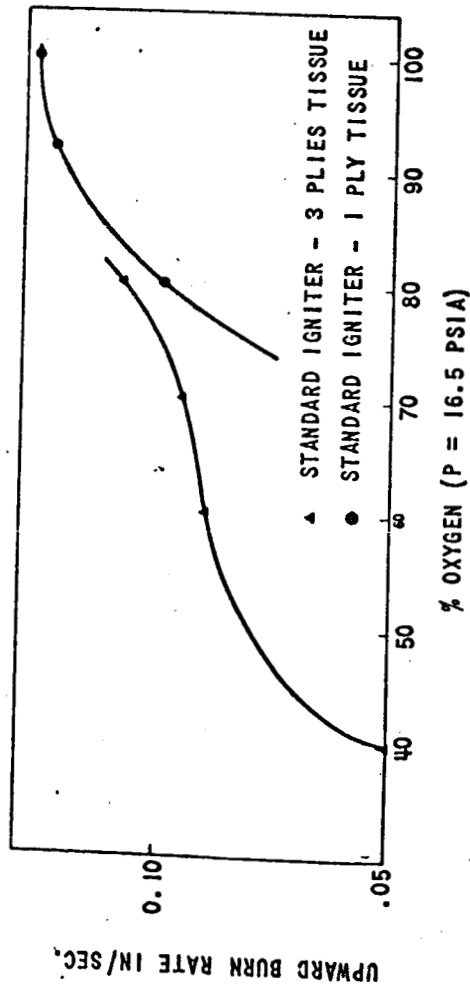
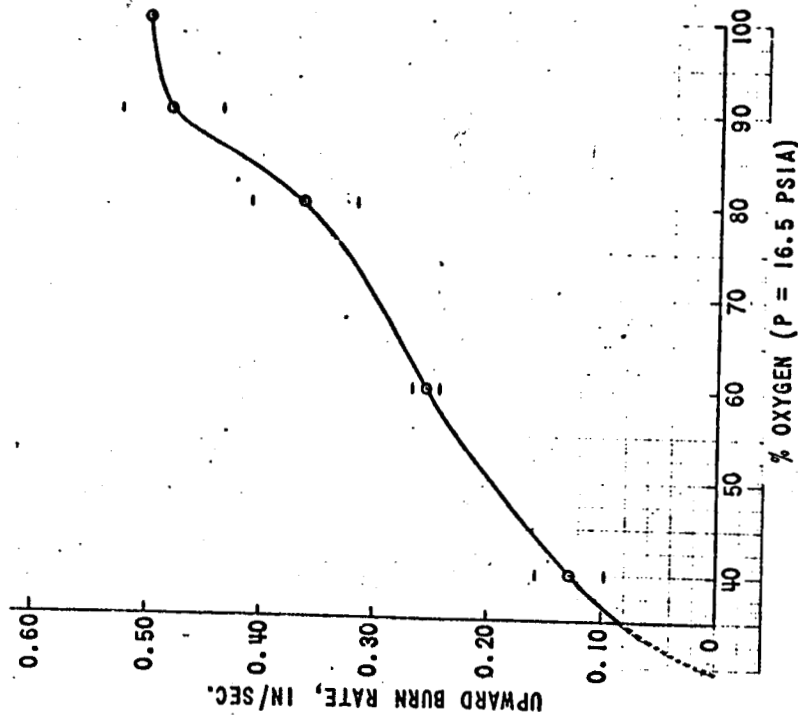
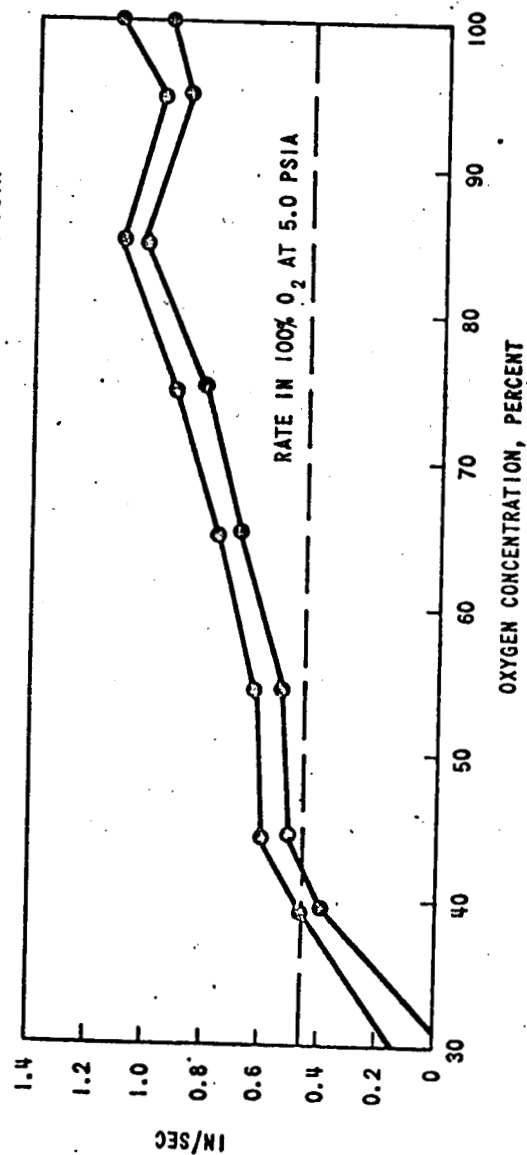
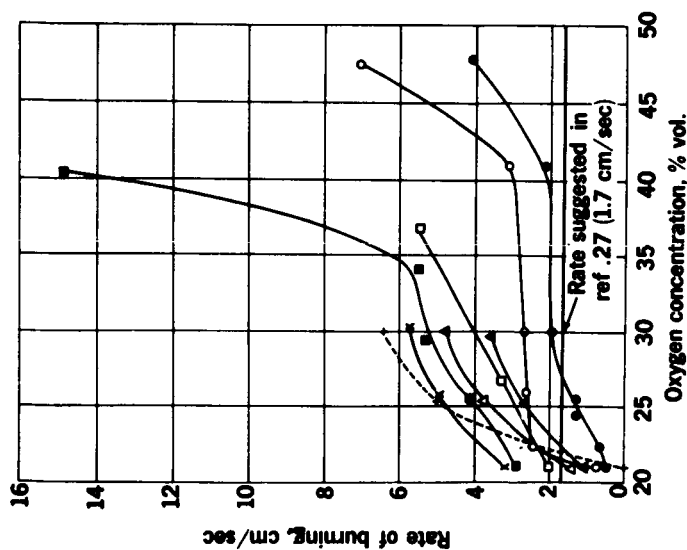


FIGURE 5 - COMBUSTION RATE OF DC 7141
SILICONE RESIN/181 GLASS FABRIC
LAMINATE (0.040-IN. THICK) (REF. 9)

FIGURE - UPWARD PROPAGATION OF 0.005 INCH TEFLON IN VARIOUS
O₂/N₂ MIXTURES AT A TOTAL PRESSURE OF 16.5 PSIA



UPWARD BURNING



- Blue melton cloth
- x— Green cotton drill
- ▲— Khaki cotton drill
- White cotton drill after washing
- Blue uniform serge
- △— Green cotton drill with flame retardant
- +— Khaki cotton drill after washing
- ◇— Wool - Terylene mixture (45-55 %)

FIGURE 20.—Variation of burning rate with oxygen concentration. (AFTER COLEMAN.⁴⁷)

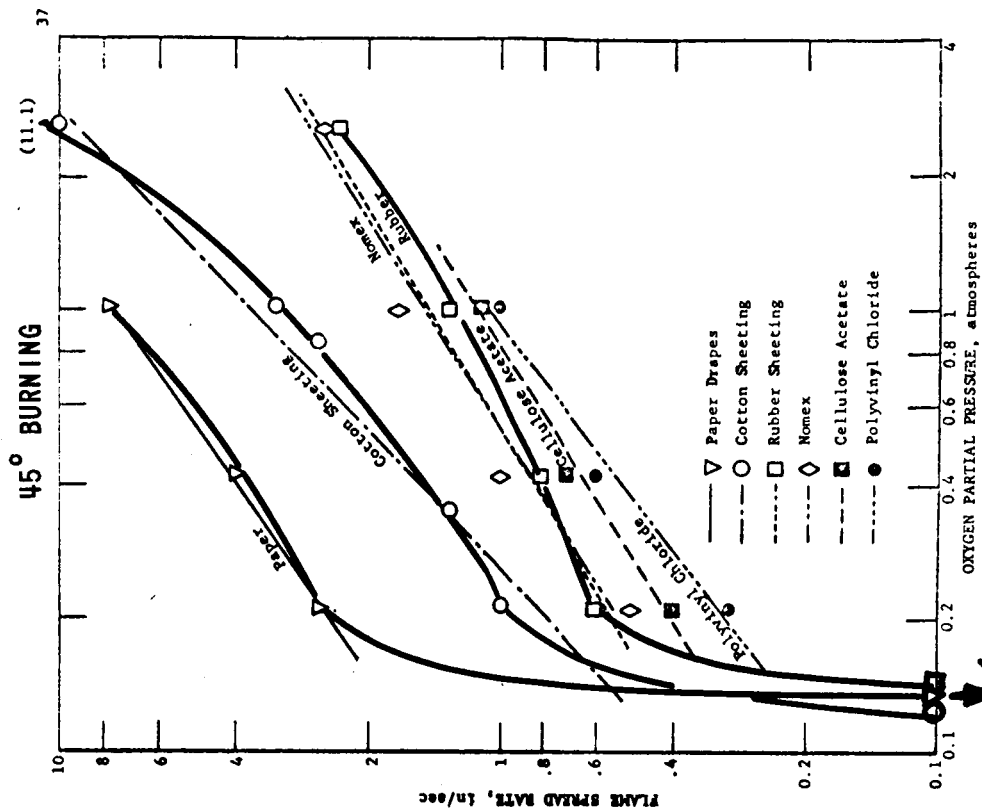


FIGURE 12.—Variation of flame spread rate with the partial pressure of oxygen for various materials in oxygen at 0.21 to 2.52 atmospheres total pressure.

PLUS POINTS OF ZERO FLAME SPREAD

SHEET 3 - BURNING OF A VARIETY OF MATERIALS IN O₂ ENRICHED ATMOSPHERES (1 & 8)

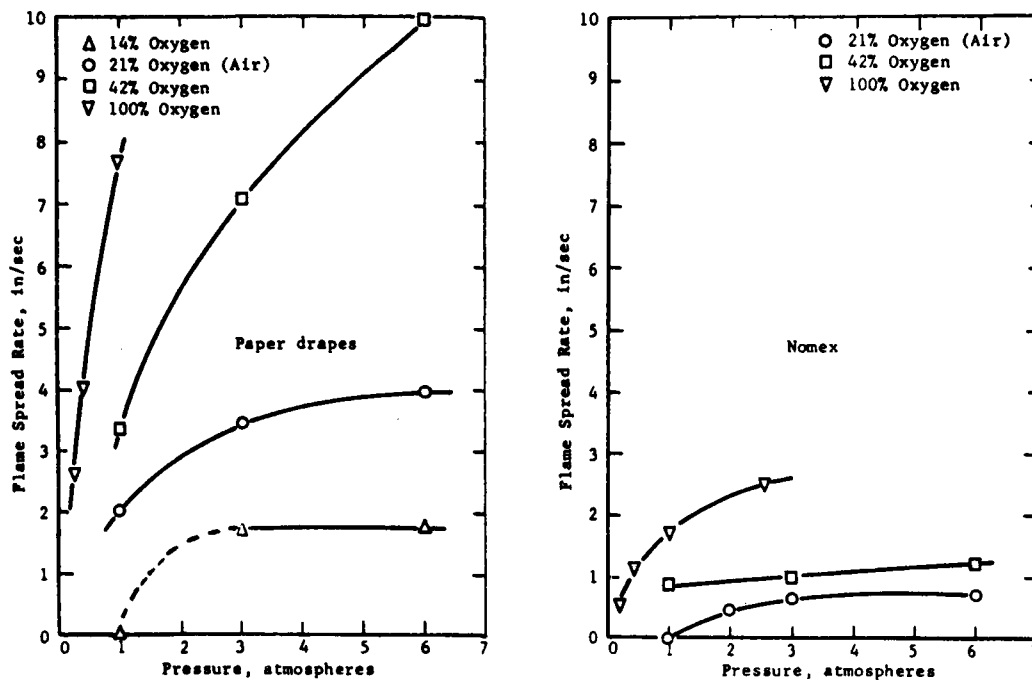


FIGURE 9. - Flame spread rates of Sanidrape (paper drapes) and Nomex in various oxygen-nitrogen mixtures at various total pressures.

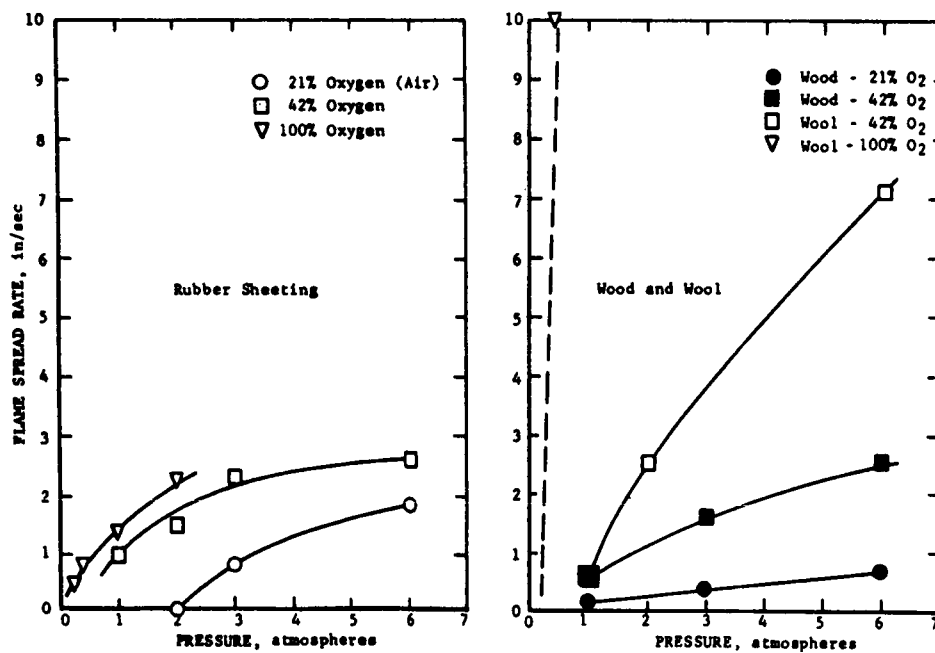
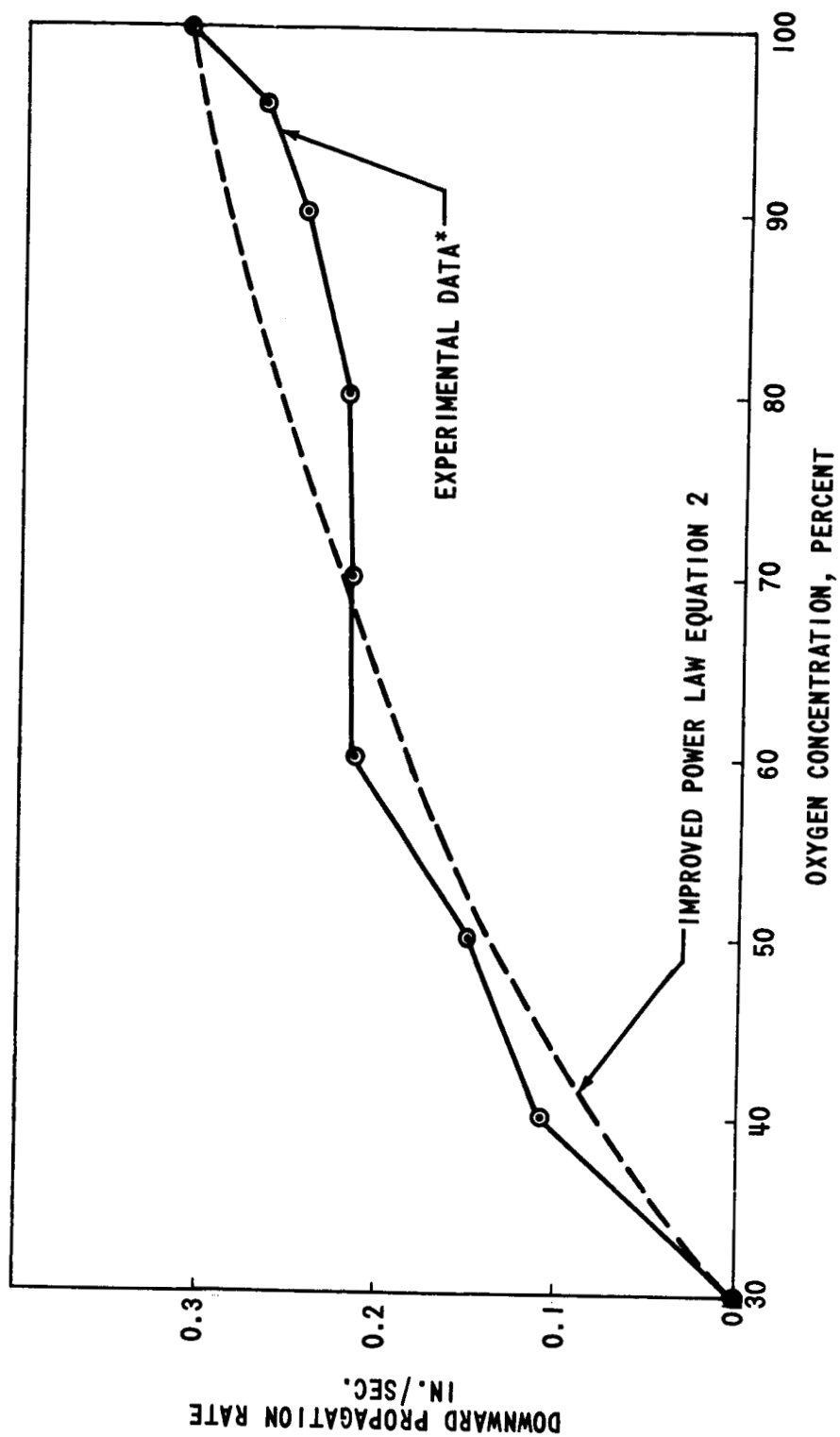


FIGURE 10. - Flame spread rates of rubber sheeting and wool (open symbols) or wood (closed symbols) materials in various oxygen-nitrogen mixtures at various total pressures.



SHEET 5 - POWER-LAW EQUATION AND EXPERIMENTAL DATA DOWNWARD
PROPAGATION OF 0.005 INCH NOMEX IN VARIOUS O_2/N_2 MIXTURES
AT A TOTAL PRESSURE OF 16.5 PSIA

* EXPERIMENTAL DATA FROM NASA MSC (REFERENCE 17)

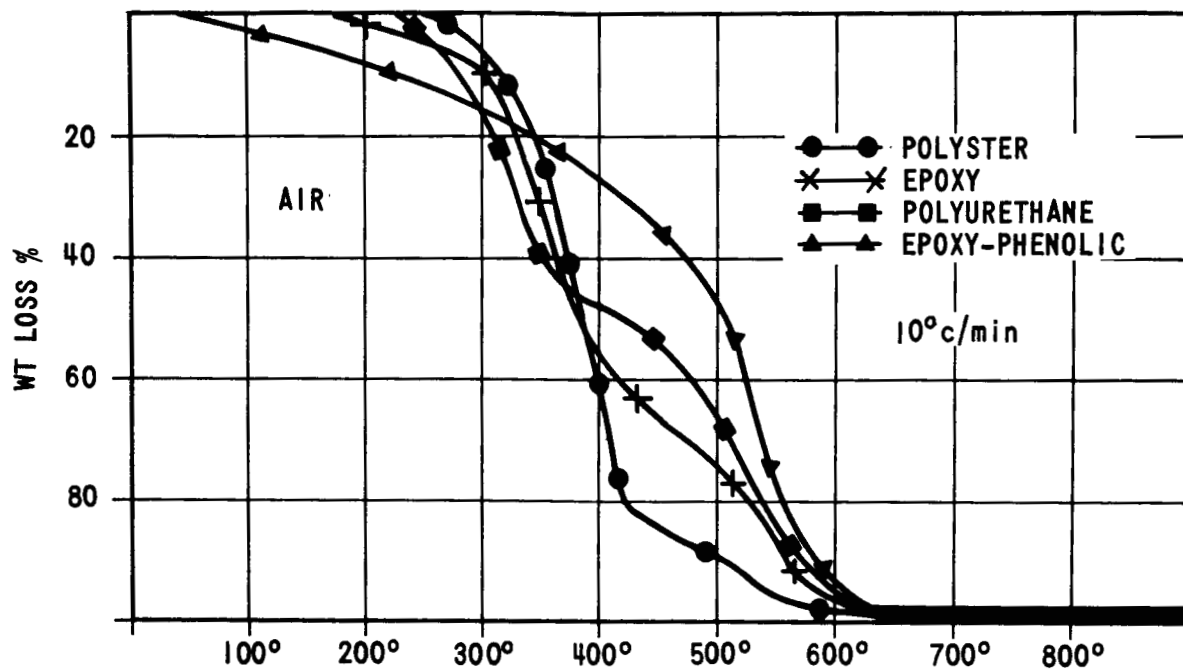


FIGURE 6 - PROGRAMMED THERMOGRAVIMETRIC CURVES (IN AIR)

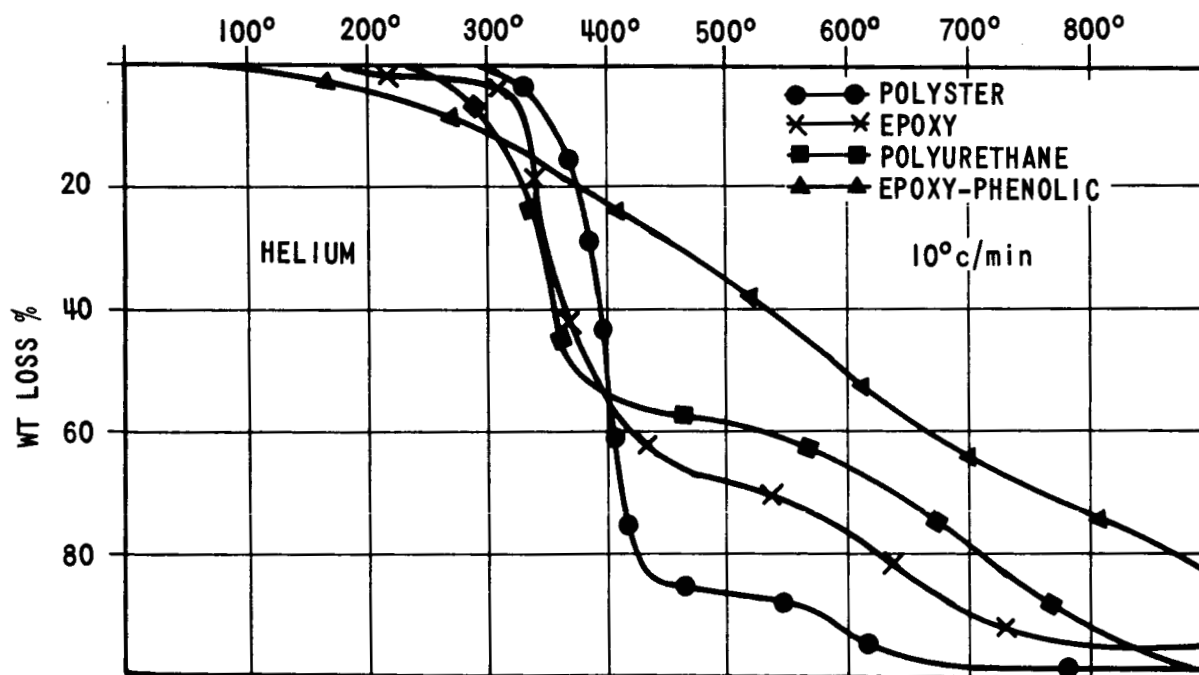
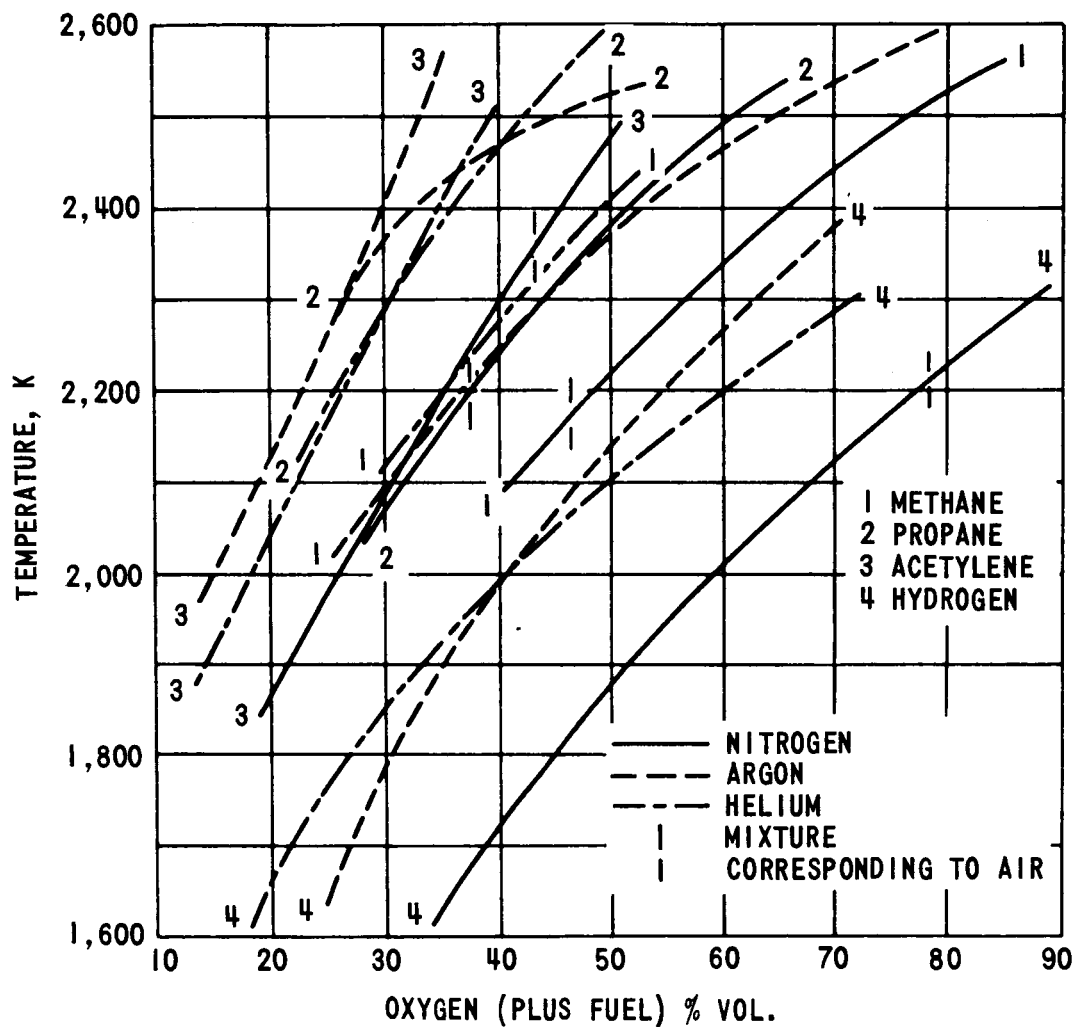
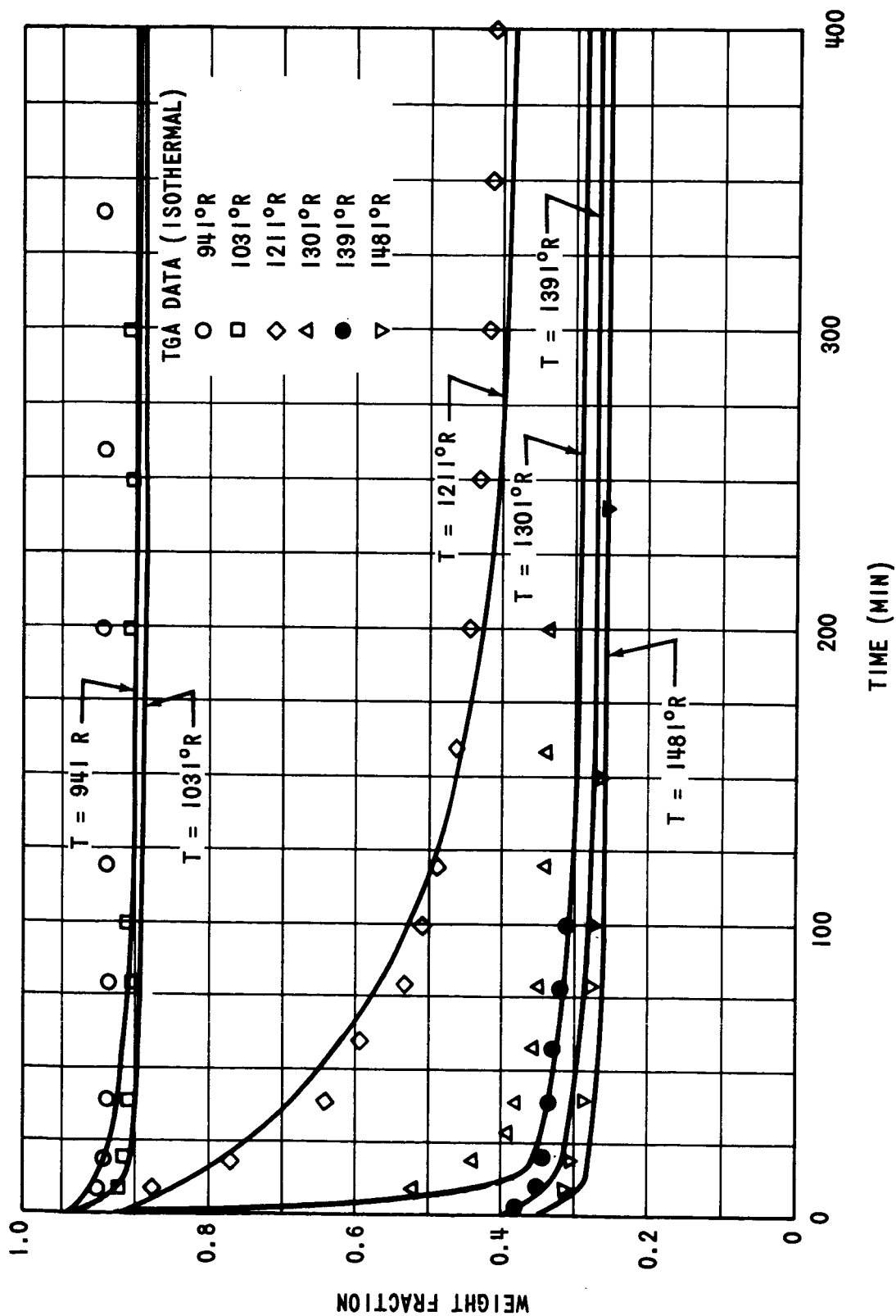


FIGURE 7 - PROGRAMMED THERMOGRAVIMETRIC CURVES (IN HELIUM)



SHEET 7 - FLAME TEMPERATURES IN VARIED INERT DILUENTS
(AFTER E. M. ROTH, CHAPTER 3 OF REF. 8)



SHEET 8 - RATE OF PYROLYSIS AS FUNCTION OF TEMPERATURE⁽²³⁾

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